Development of a new type of high pressure calorimetric cell, mechanically agitated and equipped with a dynamic pressure control system: Application to the characterization of gas hydrates

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A novel prototype of calorimetric cell has been developed allowing experiments under pressure with an *in situ* agitation system and a dynamic control of the pressure inside the cell. The use of such a system opens a wide range of potential practical applications for determining properties of complex fluids in both pressurized and agitated conditions. The technical details of this prototype and its calibration procedure are described, and an application devoted to the determination of phase equilibrium and phase change enthalpy of gas hydrates is presented. Our results, obtained with a good precision and reproducibility, were found in fairly good agreement with those found in literature, illustrate the various interests to use this novel apparatus.[http://dx.doi.org/10.1063/1.4848955]

I. INTRODUCTION

Some thermodynamic properties of fluids (e.g., phase transition temperature, phase change enthalpy, and isobaric heat capacity) are accessible by using calorimetric techniques.[1–3] In the case of pure substances, these measurements can be easily performed with classical calorimetric cells.[4–7] However, to perform experiments with multiphasic and multicomponents systems, particularly when these complex systems are handled under pressure conditions, classical calorimetric cells are not adapted. Special features, such as a sufficient agitation of the fluid(s) and the possibility to control the pressure inside the cell, are required in order to provide accurate results.

The solubilization of a gas only by diffusion in a static liquid is an extremely slow process and this phenomenon can create, if the cell is not agitated, a concentration gradient in dissolved gas from the liquid surface (high concentration) to the bottom of the cell (low concentration). Therefore, to improve the reliability of measurements performed with soluble gases (e.g., carbon dioxide, hydrogen sulfide), an agitation system is suitable to allow both a rapid and uniform solubilization of the gas into the solution. In addition, for measurements made with dispersed systems (i.e., emulsions or solid/liquid dispersions), the presence of such an agitation keeps the analyzed medium in a homogenous phase (no sedimentation or breaking of the emulsion which may distort the analysis). For chemistry applications or safety issues, it is sometimes necessary to study thermal effects generated by a chemical reaction carried out under pressure[8,9] in a semi-continuous mode (i.e., the first reactant is placed initially in the cell, and the second is progressively introduced *in situ* into the cell to react with the first one); agitation is also required.

For the crystallization of compounds occurring under pressure by a combination of both liquid and gas phases, such as the formation of clathrates compounds or gas hydrates,[10–12] stirring is very useful to renew the contact surface between the liquid and gas phases thus preventing the formation of a solid crust at the interface. The formation of this crust on the liquid surface occurs with various gas hydrates systems (e.g., those formed with methane or CO_2 with pure water) and significantly impacts the gas dissolution process, the water conversion, and the hydrate formation.[13–15]

In addition to agitation problems, a dynamic control of the cell pressure offers the possibility to ensure a gas flow through the cell (at controlled pressure or flow). This option is very useful for: (i) purging the cell (e.g., to remove any trace of air in the system at the beginning of the experiment detailed in this paper); and (ii) injecting *in situ* a liquid or a gas reactant while measuring and/or controlling the pressure inside the cell during the experiment (e.g., for process safety studies). This option also helps to maintain a given pressure in the cell or to compensate any pressure variations due to gas absorption or desorption during the reaction, occurring for instance during the formation and the dissociation of gas hydrates.

Numerous calorimetric methods and different apparatus (e.g., Differential Scanning Calorimetry,[16] spectrocalorimetry in reaction calorimeters,[17] Fast-scanning calorimetry,[18] and others) have already been proposed, developed, and tested for various applications. For further details of calorimetric techniques, thermoanalytical instrumentation, and applications, general valuable information can be found elsewhere.[19,20]

This paper presents a novel prototype of calorimetric cell developed in our laboratory, which combines the three characteristics discussed above: (i) the possibility to perform

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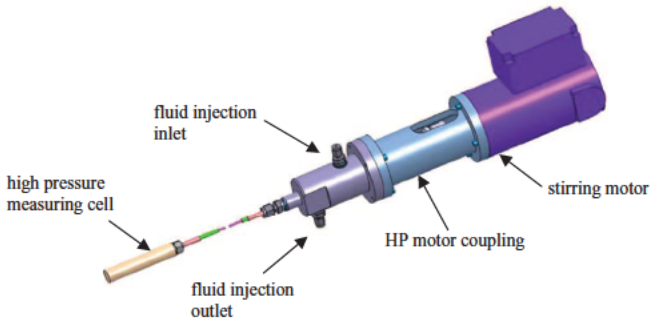

FIG. 1. Schematic representation of the prototype.

experiments under pressure (P < 20 MPa); (ii) the *in situ* mechanical agitation; and (iii) the dynamic control of the pressure of the cell. The aim of our work was then to first develop the cell prototype, then to calibrate it in temperature and enthalpies, and finally to use it for gas hydrate studies (which is a relevant practical-case in which all the potentialities of this cell are well illustrated). Such a device, which opens a very large field of applications, was recently patented by Torré *et al.*[21]

The paper is organized as follows. After a brief recall of the calorimetry basis, a detailed presentation of the new prototype is made in which the technical description of the prototype and the calibration procedures are described. Finally, an application of this new device to obtain phase equilibrium data of gas hydrates is presented.

II. EXPERIMENTAL

A. Description of the experimental apparatus

The prototype of calorimetric cell presented in this paper allows thermodynamic and calorimetric properties measurements of systems (fluids, suspensions), with a large volume of sample analyzed, under pressure and agitated conditions A schematic representation of the system is shown in Fig. 1.

The measurement cell (total volume of $\sim$ 7 cm^3) is located at the bottom of a well of 17 mm diameter and 550 mm deep. The wellhead, which is the upper part of the prototype, is positioned at the top of the well of the calorimeter (Fig. 2(c)).

On the upper part of the wellhead, a 4-lobes ring ensures a safe sealing for the passage of the rotating shaft. A clamping system allows connecting the shaft coming from the cell and the shaft coming from the agitation motor. The fluids are introduced or released into the cell by means of two nozzles located on the lateral parts of the whellhead (Fig. 3). To avoid any shunt between the fluid inlet and outlet, a O-ring inserted into an anti-shunt system creates two cavities into the whellhead, one for the fluid inlet and the one for the fluid outlet, as shown in Fig. 3.

The measuring cell is connected to the wellhead by means of two concentric tubes in which is inserted the agitating shaft. The space between the agitator shaft and the first tube is used for the admission of the fluid to the cell, and the annular space between these two concentric tubes allows circulating the fluid from the cell to the outlet (Fig. 3). Note that

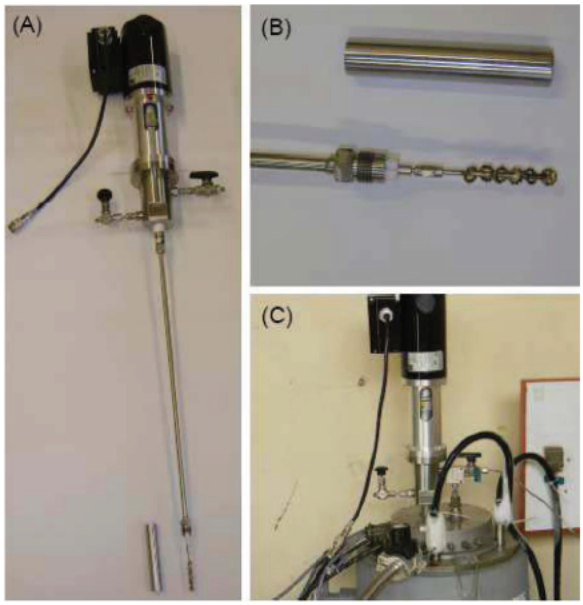

FIG. 2. Photographs of the prototype: (a) full prototype (wellhead, tubes, and measuring cell); (b) high pressure measuring cell and its own stirring system; and (c) prototype disposed on a Setaram BT 2.15 calorimeter.

the direction of the fluid flow is completely reversible. This possibility to have an inlet-outlet gas flow into the cell allows insuring a pressure control into this system. The agitation in the measuring cell is performed by a rotating system easily removable from the shaft. The stirrer is a handmade multiple-impeller agitator composed by a shaft where staggered star washers (Fig. 2(b)) have been welded. This agitator can rotate until 200 RPM.

A general view of the experimental set-up is presented schematically in Fig. 4.

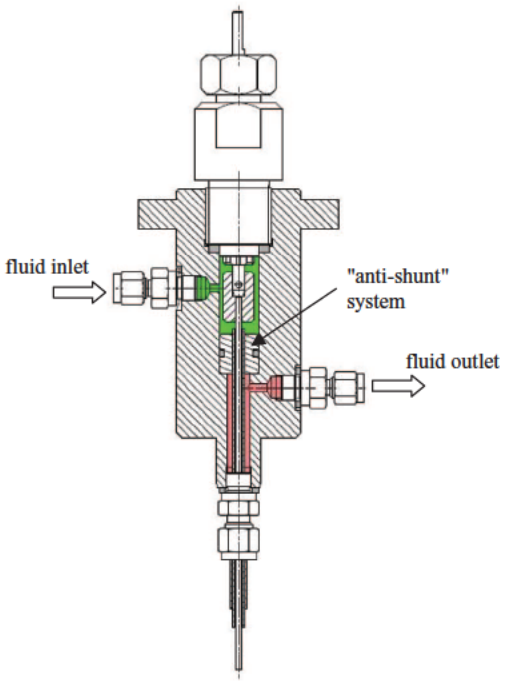

FIG. 3. Schematic representation of fluid flow.

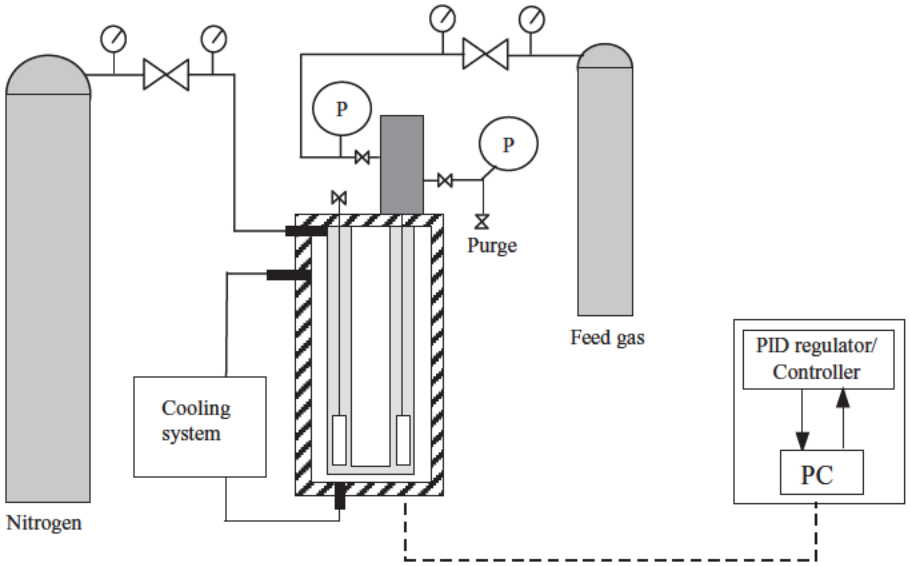

FIG. 4. View of the complete apparatus.

The high pressure measuring cell is placed directly in one of the two calorimetric wells, with the reference cell in the other well. The reference cell is filled with nitrogen at 2 bar to avoid water condensation problems at low temperature. In a similar way, the calorimetric sensors are swept by nitrogen during all the experiments. As described elsewhere,[22] instead of cooling the calorimeter by vaporization of liquid nitrogen (as proposed in the initial BT 2.15 configuration), the system was modified and connected to an external cryothermostat which maintains a circulation of ethanol in the calorimeter jacket. The temperature stability of the coolant is ± 0.01 K. All the calorimeter block where the two cells are located can thus be cooled down to a temperature of -30 °C. The high pressure measuring cell is connected to a high pressure panel: a feed gas cylinder containing carbon dioxide (in this case), valves, fittings, etc. A pressure-reducing valve allows the gas to be charged into the cell at the desired pressure with a precision of ± 0.1 bar. Two digital manometers (Leo II model from Keller) were used to measure the pressure with a precision of ± 0.1 bar upstream and downstream the measuring cell. Two precision valves, each located just after the digital manometers, allow adjusting the pressure at the desired value in order to compensate any pressure variations due to gas consumption (or release) during hydrate formation (or dissociation). Note that during all the experiment, the pressure is maintained constant with a precision ± 0.5 bar around the setpoint.

B. Materials used

All the organic products used for the calibration are supplied by Sigma Aldrich with a purity superior to 99.7% for cyclohexane and superior to 99% for n-dodecane, n-tetradecane, and n-hecadecane. For all experiments, the quantities of material introduced in the cell were weighted using an electronic balance with a precision of ± 0.001 mg. We use ultra pure water (resistivity of 18.2 MΩ · cm) produced in our laboratory by a water purification system from ELGA Labwater (France). The gases used in the experiments are nitrogen and carbon dioxide supplied by Linde gas with a purity of 99.999% and 99.995%, respectively.

C. Calibrations of the prototype in temperature and enthalpy

Calorimetric measurements such as phase transition temperature and heat associated require first a precise temperature and enthalpy calibration. For this purpose, the calibration procedure was performed using five pure components namely water, cyclohexane, n-dodecane, n-tetradecane, and n-hexadecane, for which melting points and enthalpies of fusion are well known (National Institute of Standards and Technology data base). These calibrating fluids have been chosen particularly because: (i) their melting point cover a temperature range corresponding to the domain investigated for the practical application presented in this paper in Sec. III (i.e., the study of CO_2 hydrate formation/dissociation); (ii) the range of enthalpy covered by the different compounds analyzed is very large (from 30 to 300 $J\,g^{-1}$). The properties of each calibrating substance, in terms of melting temperature and enthalpy of fusion, are listed in Table I and a type-curve (obtained with

TABLE I. Phase change properties of pure components used for the calibrations (data from the National Institute of Standards and Technology data base) and comparison to our experimental data.

	Melting point (°C)		Enthalpy of fusion
	Ref.	Our data	($J\,g^{-1}$)
Water	0.00 ± 0.05	0.1 ± 0.2	333 ± 3
Cyclohexane	6.5 ± 0.3	6.8 ± 0.2	32.6 ± 0.3
N-dodecane	-9.7 ± 0.3	-9.8 ± 0.2	214 ± 2
N-tetradecane	5.6 ± 0.9	5.3 ± 0.2	227 ± 2
N-hexadecane	18 ± 1	18.1 ± 0.2	227 ± 2

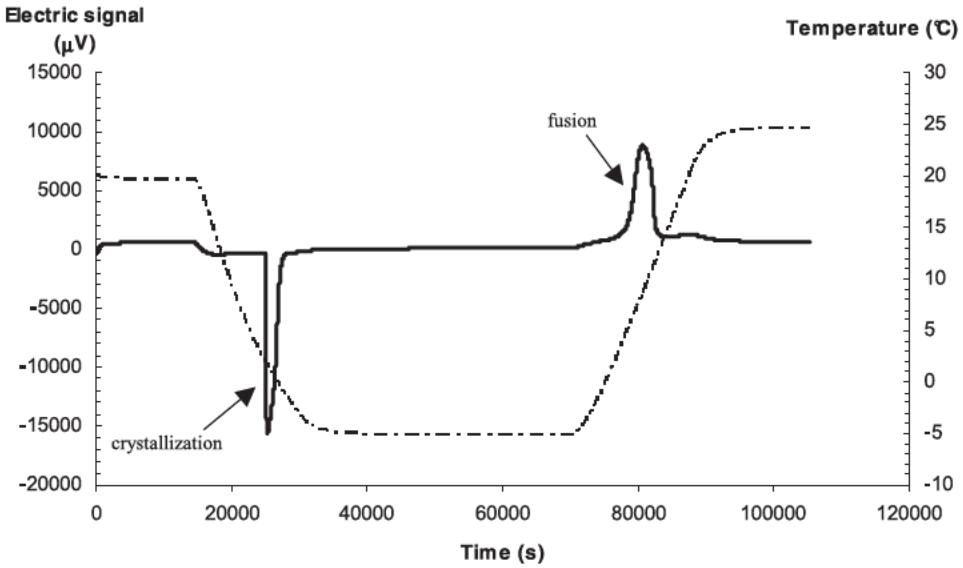

FIG. 5. Calorimetric trace obtained with n-tetradecane.

n-tetradecane) is presented in Fig. 5. Note that for all experiments, the calibration was done at atmospheric pressure and without agitation.

To perform the calibration experiments, the measuring cell was first systematically filled with the same volume for each compound, i.e., 4.5 cm^3, to obtain exactly the same liquid level into the cell. Note that the quantity of each material has been weighed at 20 °C using densities available in literature.[23] Then, the cell was sealed, introduced in the calorimeter, and cooled at $\sim$ 0.1 °C/min to crystallize the product. After the temperature was stabilized at a suitable temperature (lower than the crystallization point, e.g., −5 °C in Fig. 5), the sample was heated progressively at 0.1 °C/min from −5 °C to 25 °C to melt the solid formed and thus determine precisely both the corresponding fusion temperature and enthalpy. As shown in Fig. 5, the first peak (exothermic phenomenon) visible during the cooling period correspond to the crystallization of the standard, and the second (observed during the heating phase) is attributed to its fusion. For this temperature calibration, taking into account the method to determine the phase transition temperature from the calorimetric trace (from the onset temperature) and the reproducibility of the experiments, the uncertainty is estimated to ±0.2 °C. The results of the temperature calibration are presented in Table I.

The enthalpy calibration leads to determine the sensitivity of the calorimetric sensors. This allows to convert the direct information provided by the sensors, i.e., an electrical force (expressed in μV, see Sec. II A), to a power (generally expressed in mW). In this procedure, the enthalpy of fusion (expressed here in $J\,g^{-1}$) for the calibrating fluids is plotted versus the surface area of the peak (expressed in $\mu V\,s\,g^{-1}$) at the calorimetric trace and corresponding to the phase transition. As shown in Fig. 6, the calibration curve obtained for

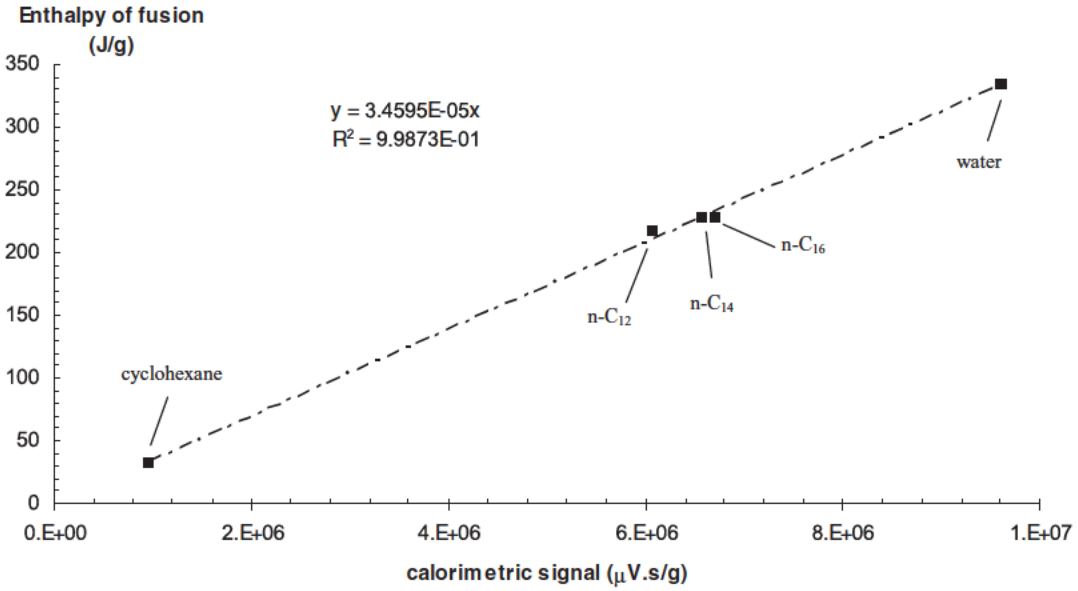

FIG. 6. Results of the enthalpy calibration procedure.

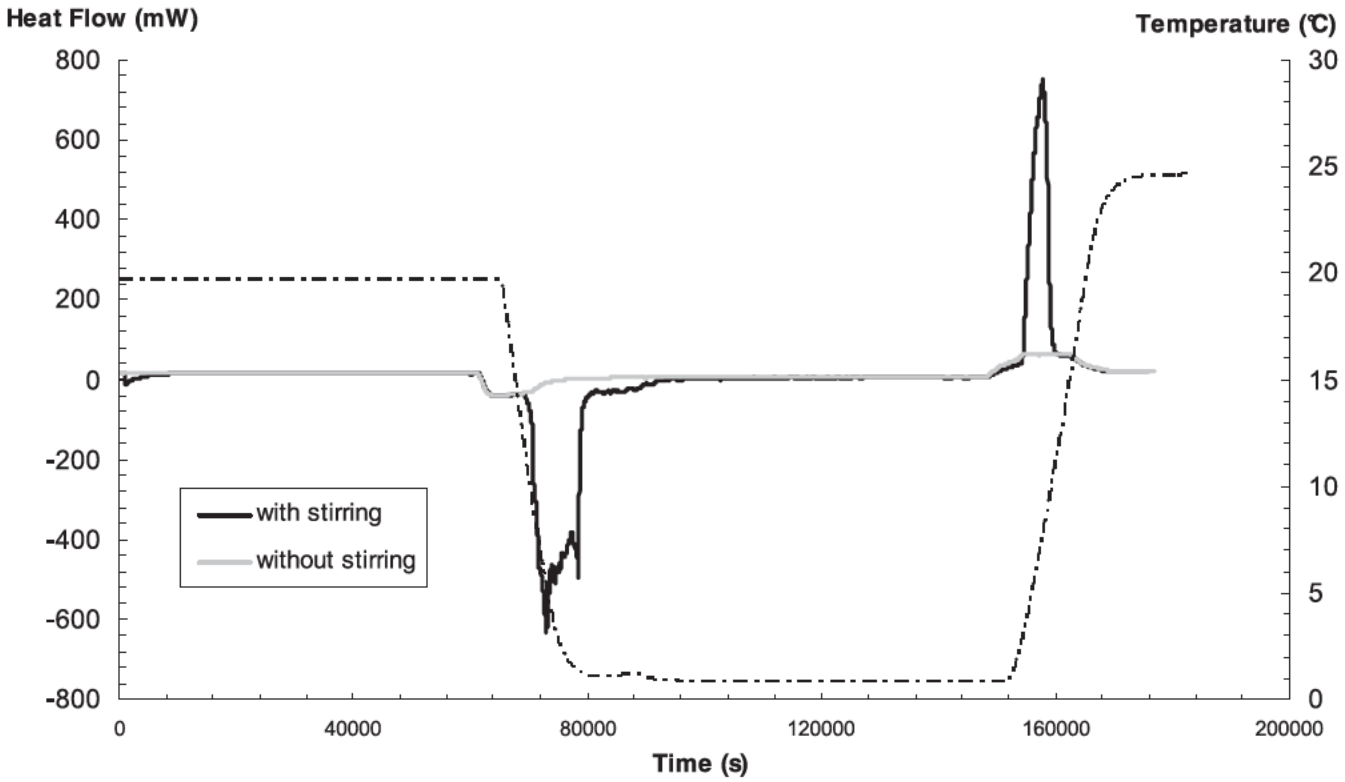

FIG. 7. Calorimetric trace of the formation/dissociation of the carbon dioxide hydrate.

enthalpies is almost a perfect line which goes through zero. The sensitivity of this prototype is evaluated to (3.46 ± 0.05) $.10^{-5}$ J μV^{-1} s^{-1}, leading to an uncertainty of $\pm 2\%$ for the determination of enthalpies.

III. APPLICATION TO THE CHARACTERIZATION OF CARBON DIOXIDE HYDRATE FORMATION

The prototype was used to obtain thermodynamic properties of gas hydrates, particularly the CO_2 hydrate. For more information about these structures, the reader is invited to consult Sloan and Koh[24] for a general background on these compounds, and to Uchida *et al.*[25] for data and properties of the CO_2 hydrates. In short, gas hydrates are non-stoechiometric inclusion compounds formed by a lattice structure, composed of water molecules (named *host* molecules) linked together by hydrogen bonding, and stabilized by encapsulating a variety of small molecules (named *guest* molecules). The measurement of thermodynamic or thermophysical data of gas hydrates is important in various domains—where these structures are usually met—such as petroleum engineering, flow-assurance, environment, CO_2 capture and storage, energy, etc.[24] The practical case detailed in this section is devoted to the formation and then the dissociation of the carbon dioxide hydrate. The protocol used is described in the following and illustrated in Fig. 7.

An exact quantity of ultra-pure water is directly introduced in the high pressure measuring cell. The prototype is then placed in one of the calorimetric wells the other receiving the reference cell filled with nitrogen at 2 bar (see Sec. II B) and connected to the CO_2 storage vessel. A gas sweep is performed at low pressure to avoid any trace of air in the system. When the experiment is done under agitated conditions, the stirring is at this moment with a constant agitator rotation speed of 150 RPM. The system is pressurized at the desired pressure with CO_2 (the pressure is set to 30.5 bar for these experiments) and maintained at constant pressure at 20 °C during $\sim$ 18 h. The temperature is then decreased form 20 to 0.9 °C at a cooling rate of 0.1 °C/min to bring the system in the CO_2 hydrate metastability zone (i.e., the pressure-temperature region where the CO_2 hydrate should form). Note that the temperature is always maintained above zero to avoid any risk of ice formation. The temperature is then maintained constant at 0.9 °C during $\sim$ 20 h. Finally, the temperature is from 0.9 to 25 °C at 0.1 °C/min to dissociate the hydrate formed, and the temperature is finally stabilized at 25 °C.

To illustrate the effect of the agitation, Fig. 7 shows two experiments carried out exactly in the same conditions except the presence of agitation: one of the experiment is carried out under agitated conditions (agitation speed maintained at 150 RPM), and the other one is done in quiescent—or static—conditions (no agitation). It can be clearly demonstrated that no crystallization is observed in quiescent conditions. In contrary, in agitated conditions, the CO_2 hydrate forms easily during the cooling ramp of temperature (crystallization beginning at P = 30.5 bars and T = 12°C), the presence of agitation triggering the hydrate formation by breakage of the crystallization metastability. To maintain a constant agitator speed, the intensity of the motor is increasing. During the crystallization, the torque imparted in the agitator by the motor is increasing progressively to agitate the hydrate slurry which is thickening into the cell. Note that the system is

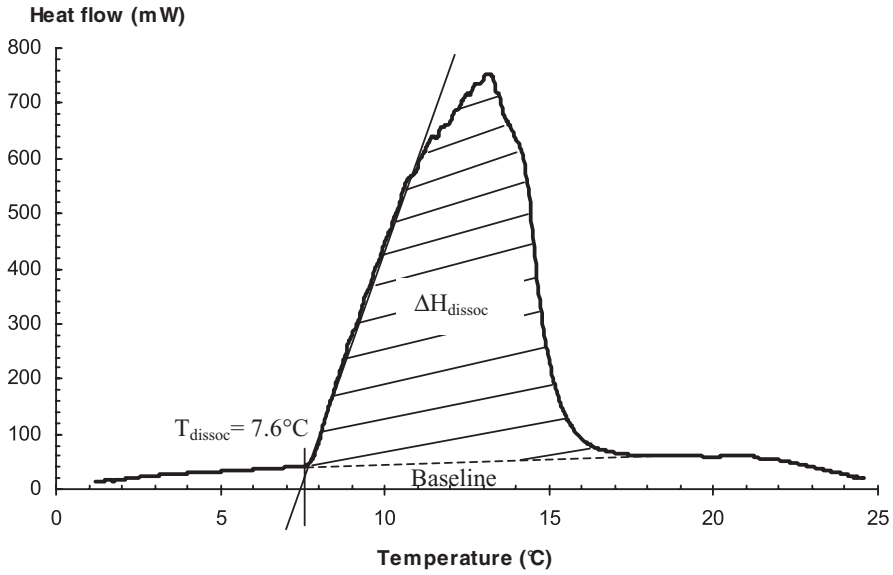

FIG. 8. Determination of both enthalpy and temperature of dissociation of the carbon dioxide hydrate.

maintained agitated since the intensity of the motor remains inferior to its safety limit, equivalent to a torque of the motor about 2 N m. Therefore, the agitator generally stops close to the maximum of the exothermic peak meaning that at this point there is likely to have very few free-water in the system hydrate.

Both enthalpy and temperature of dissociation of carbon dioxide hydrate were directly deduced from the calorimetric trace. The dissociation temperature at the given pressure (here 30.5 bar) corresponds to the equilibrium point where the hydrate begins to release the gas entrapped in the water cavities. The dissociation temperature corresponds to the intersection between the base line and the inflectional tangent at the ascending peak slope (Fig. 8), while the peak area highlighted in Fig. 8 represents the amount of heat exchanged during the phase transition. The enthalpy of dissociation ΔH_{dissoc} is then calculated by dividing this area (expressed in J) by the amount of carbon dioxide trapped in hydrate assuming that the hydration number (denoted n) of the carbon dioxide hydrate (CO_2-n.H_2O) is equal to 7.3,[25] and a total conversion of water to hydrate.

Three experiments were conducted to test the reproducibility of the method. As proven by the results obtained and listed in Table II; the reproducibility is fairly good.

The Fig. 9 plots our result in terms of dissociation temperature at 30.5 bars (average of the three experiments carried out) on the three-phasic equilibrium line where gas, liquid, and CO_2 hydrate coexist. The equilibrium data of reference are both experimental[26–28] and numerical (data obtained using the well-known CSMGem program of the Colorado School of mines, from Sloan and Koh).[24]

The comparison between our data and those from other authors shows a very good agreement and proves the validity of the approach and of the system used. Regarding the enthalpy measurements, our results (62 ± 3 kJ mol^{-1}) agree with the available literature such as those of Anderson[29] who found this enthalpy to vary between 63.6 ± 1.8 kJ mol^{-}1 and 57.7 ± 1.8 kJ mol^{-1} between the two quadruple points, and those obtained more recently by Sabil *et al.*[30] with a value of 62.48 kJ mol^{-1} in very similar conditions of pressure (P_{CO2} = 30 bar instead of 30.5 bar).

TABLE II. Enthalpy and temperature of dissociation of carbon dioxide hydrate at P = 30.5 bar.

	T (°C)	Enthalpy (kJ mol^{-1})
Test 1	7.5 ± 0.2	62 ± 3
Test 2	7.6 ± 0.2	60 ± 3
Test 3	7.7 ± 0.2	61 ± 3

IV. CONCLUSIONS

A novel prototype of calorimetric cell has been developed. The technical details of the system and typical results were presented. It was demonstrated that this invention allows performing experiments under pressure, with an *in situ* agitation system and a dynamic control of the pressure inside the cell. The prototype was well calibrated in temperature and enthalpies with various pure substances used as standards, covering a range of temperature (from −10 to 20 °C) and enthalpies (from 30 to 300 J g^{-1}). The system has been used to perform experiments with gas hydrates, particularly to characterize CO_2 hydrates. It was demonstrated that the presence of the agitation was necessary to crystallize the hydrates in the conditions tested. The reproducibility of the experiments was fairly good, and the dissociation temperature and enthalpy were found in good agreement with other references. The use of such a system thus opens a wide range of potential practical applications for determining properties of complex fluids in both pressurized and agitated conditions.

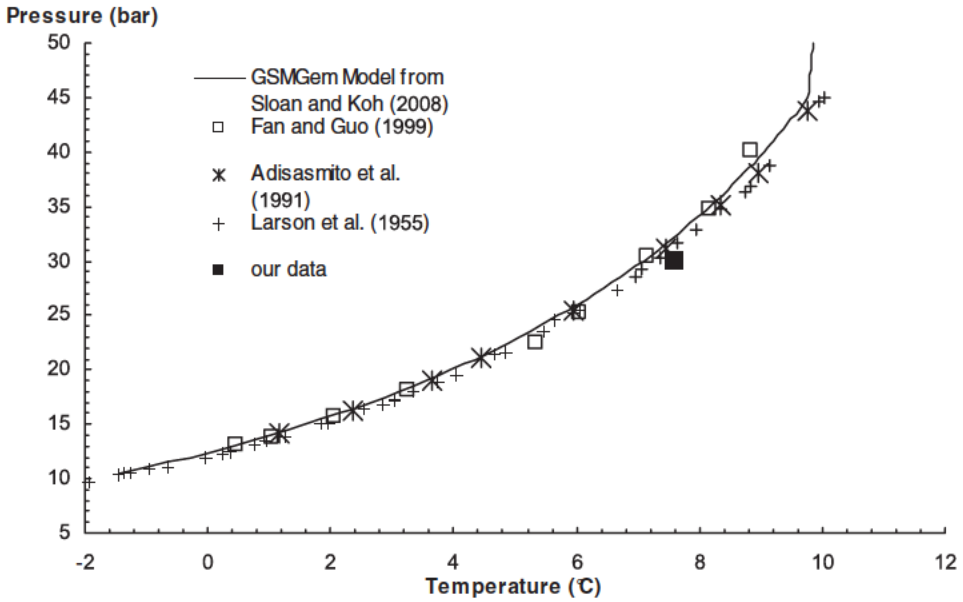

FIG. 9. Experimental temperature of carbon dioxide hydrate dissociation (P = 30.5 bars) and comparison to literature data of Sloan and Koh,[24] Fan and Guo,[26] Adisasmito[27], and Larson.[28]

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